

2. THERMODYNAMIC PROPERTIES OF ALTERNATIVE AGENTS

Giann C. Yang and Brett D. Breuel
Building and Fire Research Laboratory

2.1 Introduction

Depending upon their applications, current halon 1301 (CF_3Br) bottles are normally filled to about half of the bottle volume, and the bottle is then pressurized with nitrogen to 4.1 MPa (600 psig) at room temperature. The purpose of using the pressurization gas is to expedite the discharge of the agent and to increase the penetration distance of the agent during discharge. However, this driving force, *i.e.*, the total pressure in the bottle, will vary depending on the ambient temperature because the vapor pressure of the agent and the solubility of the pressurization gas in the liquid agent vary with temperature. The current military specification (MIL-C-22284A) for halon 1301 containers stipulates that the container should have a proof pressure of 9.62 MPa (1400 psig), a burst pressure of 12.37 MPa (1800 psig), and a frangible disc that will rupture at a pressure between 8.59 MPa (1250 psig) and 9.62 MPa (1400 psig) at 70 °C. In order to explore the possibility of using existing halon 1301 bottles for "drop-in" replacement agents or to provide safety guidelines on bottle design for the alternative agents, two important tasks are to determine (1) the solubility of the pressurization gas in the liquid agent and (2) the final pressure of the vessel when exposed to different ambient temperatures.

In the first task, some thermodynamic properties of the core agents listed in Section 1 were measured. Halon 1301 was also included in this study for the purposes of reference and comparison with the alternative agents. In particular, the objective was to determine the final equilibrium pressure in the bottle when the bottle, filled with either a pre-determined amount of pure agent or with agent and pressurization gas, was exposed to different temperatures. Experiments on pure agents were performed in order to obtain the vapor pressure data when documented data were not available. Two pressurization gases, nitrogen and CHF_3 (HFC-23), were used in the study. Trifluoromethane (CHF_3) was explored as a pressurization gas because it itself could be used as a fire suppressing agent. Another property that makes CHF_3 a potential candidate as a pressurization gas is its vapor pressure of 4.16 MPa (606 psia) at 20 °C, which is high enough to pressurize the vessel to the appropriate level.

The second task of this study was to determine the solubility of the pressurization gas in the agent at room temperature. Specifically, the objective was to measure the amount of the gas initially used to pressurize the bottle to 4.1 MPa. This part of the study, in essence, determined the initial condition of the vessel.

For the purpose of reference, selected thermo-physical properties of pure agents are tabulated in Table 1 where MW is the molecular weight, T_b is the normal boiling point (at 0.101 MPa), T_c is the critical temperature, P_c is the critical pressure, p_{sat} is the saturation vapor pressure at 25 °C, ρ_c is the critical density, ρ_l is the saturated liquid density at 25 °C, $C_{p,l}$ is the isobaric liquid heat capacity at T_b , $C_{p,2}$ is the isobaric liquid heat capacity at 25 °C, and h_{fg} is the latent heat of vaporization at T_b . The properties of CHF_3 are also included in the table. One mixture is included which is 60% (by mass) HFC-32 and 40% HFC-125. Table 2 lists the characteristic constants used to estimate the

Table 1. Tabulated values of selected thermo-physical properties of agents

Agent	MW (kg/mol)	T_b	T_c	P_c	P_{sat}	ρ_c	ρ_l	C_{pI}	C_{p2}	h_{fg} (kJ/kg)
		(°C)		(MPa)		(kg/m ³)		(kJ/kg K)		
HFC-236fa	0.152	-1.5 ^a	130.6 ^a	3.17 ^a	0.27 ^a	430 ^a	1356 ^b	1.114 ^c	1.179 ^c	150 ^d
FC-31-10	0.238	-2.0 ^e	113.2 ^e	2.32 ^e	0.27 ^f	600 ^e	1497 ^g	0.951 ^c	1.017 ^c	96 ^f
FC-318	0.200	-7.0 ^h	115.2 ^h	2.77 ^h	0.31 ^h	619 ^f	1499 ^h	1.009 ^h	1.098 ^h	112 ^h
HCFC-124	0.137	-13.2 ^h	122.5 ^h	3.65 ^h	0.38 ^h	565 ⁱ	1357 ^h	1.080 ^h	1.111 ^h	162 ^h
HFC-227ea	0.170	-16.4 ^j	101.7 ^j	2.90 ^j	0.47 ^k	621 ^j	1395 ^k	1.074 ^h	1.177 ^h	131 ^k
CF ₃ I	0.196	-22.0 ^l	122.0 ^m	4.04 ^m	0.49 ⁿ	871 ^m	2106 ^b	0.542 ^c	0.592 ^c	106 ^d
HFC-134a	0.102	-26.2 ^h	101.2 ^h	4.05 ^h	0.67 ^h	508 ^o	1209 ^h	1.269 ^h	1.395 ^h	217 ^h
FC-218	0.188	-36.8 ^h	72.0 ^h	2.67 ^h	0.88 ^h	629 ^f	1321 ^h	0.977 ^h	1.151 ^h	101 ^h
HCFC-22	0.087	-40.9 ^h	96.2 ^h	5.04 ^h	1.05 ^h	525 ^f	1192 ^h	1.116 ^h	1.239 ^h	229 ^h
HFC-125	0.120	-48.6 ^h	66.3 ^h	3.62 ^h	1.38 ^h	571 ^p	1190 ^h	1.107 ^h	1.358 ^h	160 ^h
HFC-32/125	0.067	-52.5 ^q	73.2 ^q	5.04 ^q	1.67 ^q	479 ^q	1040 ^q	1.449 ^c	1.763 ^c	287 ^q
CF ₃ Br	0.149	-57.8 ^h	67.0 ^h	3.95 ^h	1.61 ^h	745 ^r	1551 ^h	0.670 ^h	0.881 ^h	111 ^h
FC-116	0.138	-78.2 ^f	19.7 ^f	2.98 ^f	-	608 ^f	-	0.956 ^c	-	117 ^f
CHF ₃	0.070	-82.1 ^r	25.6 ^r	4.82 ^r	4.69 ^s	516 ^r	0.685 ^s	1.269 ^h	-	240 ^h

^aFrom Du Pont Chemicals Data Sheet, personal communication (1993)

^bEstimated by the modified Rackett method (Reid *et al.*, 1987)

^cEstimated by the method of Rowlinson (Reid *et al.*, 1987)

^dEstimated by Pitzer acentric factor correlation (Reid *et al.*, 1987)

^eFrom Daubert and Danner (1993)

^fFrom Braker and Mossman (1980)

^gFrom Brown and Mears (1958)

^hFrom Gallagher *et al.* (1993)

ⁱFrom Shankland *et al.* (1990)

^jFrom Great Lakes Chemical Corporation (1993)

^kFrom Hoechst AG, personal communication (1992)

^lFrom Kudchadker *et al.* (1979)

^mFrom Sladkov and Bogacheva (1992)

ⁿEstimated by the method of Lee and Kesler (Reid *et al.*, 1987)

^oFrom Piao *et al.* (1991)

^pFrom Allied Signal Inc. (1990)

^qFrom Allied Signal Inc. (1991)

^rFrom ASHRAE Inc. (1969)

^sFrom Platzter *et al.* (1990)

isobaric ideal-gas heat capacities (C_p^o) of all the agents used in this study. The sources of these data are also documented in Tables 1 and 2.

Table 2. Characteristic constants used to calculate C_p^o (kJ/kg K) as a function of temperature T (K); $C_p^o = A + BT + CT^2 + DT^3 + (E/T)$

Agent	A	B	C	D	E
HFC-236fa ^a	-8.05×10^{-2}	4.01×10^{-3}	-3.82×10^{-6}	1.33×10^{-9}	0
FC-31-10 ^a	-1.59×10^{-1}	4.24×10^{-3}	-4.41×10^{-6}	1.60×10^{-9}	0
FC-318 ^b	4.51×10^{-2}	3.33×10^{-3}	-3.22×10^{-6}	1.14×10^{-9}	0
HCFC-124 ^c	1.76×10^{-1}	2.12×10^{-3}	-1.00×10^{-6}	0	0
HFC-227ea ^a	-4.61×10^{-2}	3.70×10^{-3}	-3.54×10^{-6}	1.22×10^{-9}	0
CF ₃ I ^a	3.81×10^{-2}	1.53×10^{-3}	-1.70×10^{-6}	6.60×10^{-10}	0
HFC-134a ^c	-5.26×10^{-3}	3.30×10^{-3}	-2.02×10^{-6}	0	15.82
FC-218 ^d	6.88×10^{-2}	3.31×10^{-3}	-3.41×10^{-6}	1.28×10^{-9}	0
HCFC-22 ^b	1.61×10^{-1}	2.08×10^{-3}	-1.70×10^{-6}	5.28×10^{-10}	0
HFC-125 ^c	1.90×10^{-1}	2.47×10^{-3}	-1.44×10^{-6}	0	0
HFC-32/125 ^c	3.82×10^{-1}	1.62×10^{-3}	-3.85×10^{-7}	0	0
CF ₃ Br ^f	1.47×10^{-1}	1.45×10^{-3}	-1.42×10^{-6}	5.01×10^{-10}	0
FC-116 ^b	1.03×10^{-1}	3.04×10^{-3}	-2.98×10^{-6}	1.05×10^{-9}	0
CHF ₃ ^b	5.49×10^{-2}	2.97×10^{-3}	-2.62×10^{-6}	8.97×10^{-10}	0

^aEstimated by the method of Joback (Reid *et al.*, 1987)

^bFrom Yaws *et al.* (1988)

^cFrom Allied Signal Inc. (1990)

^dFrom Fang and Joffe (1966)

^eFrom Allied Signal Inc. (1991)

^fFrom Property Data Bank (Reid *et al.* 1987)

2.2 Experimental Apparatus and Procedures

The pressure-temperature relationship for pure agents and agent/pressurization gas mixtures at one fill condition (*i.e.*, the volume of the liquid agent in the vessel was fixed in all the experiments) was measured. Except for the experimental procedure, the same apparatus was used in both studies. For pure agents and agent/nitrogen mixtures, pressure measurements were determined at three temperatures, -60 °C, 22 °C, and 150 °C. For agent/CHF₃ mixtures, pressure measurements were obtained at -60 °C, 22 °C, and at the maximum temperature which did not cause the pressure to exceed the safe operating limit of the vessel (for reasons to be discussed).

A fill condition of 1/3 of the vessel volume was selected because the so-called liquid-full condition could be avoided when the vessel was heated to high temperatures. To illustrate the significance of the liquid-full condition, let us consider a PT (pressure-temperature) phase diagram for a pure substance for the purpose of simplicity and clarity. Figure 1 shows the general behavior of a pure substance. The saturation curve (or the vapor pressure curve), which represents the existence of

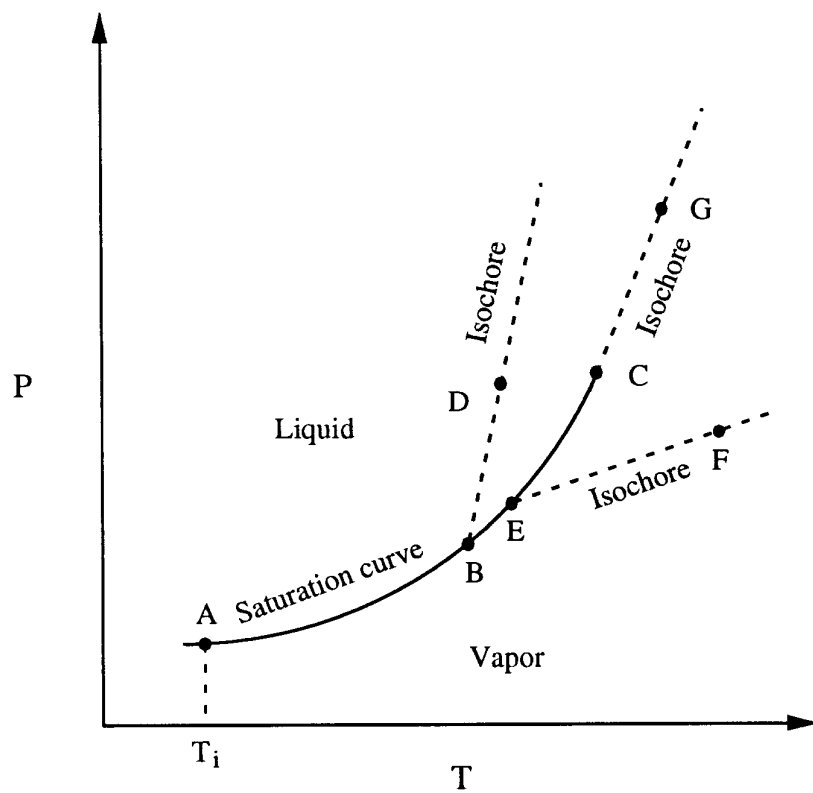


Figure 1. PT diagram showing the saturation curve for a pure substance and isochores.

two phases (vapor and liquid) in equilibrium, separates the vapor and liquid regions. The curve terminates at the critical point C . If one puts a fixed amount (M) of a liquid-vapor mixture of a pure substance in a closed vessel with a volume V at T_i (represented by point A in Figure 1) and raises the temperature of the vessel, two things will happen: the liquid vaporizes and at the same time expands. The heating process at first follows the saturation curve until a single phase state is reached. This state depends on the ratio of M to V , or the fill density (ρ_{fill}) of the vessel. If ρ_{fill} is greater than the critical density (ρ_c), continuous heating initially from point A causes the liquid-vapor interface (the meniscus) to rise because the rate of thermal expansion of the liquid is faster than its vaporization rate. Eventually, a state (point B) on the saturation curve will be reached where the liquid completely fills the vessel. This condition is termed *liquid-full*. The location of point B can be determined by identifying the temperature at which the saturation liquid density is equal to ρ_{fill} . Further heating of the vessel beyond point B can only occur in the liquid region along the liquid constant density line (or isochore), BD , corresponding to the constant ρ_{fill} . If ρ_{fill} is less than ρ_c , heating initially from point A causes the meniscus to recede due to the slower rate of thermal expansion of the liquid than its vaporization rate. The liquid eventually will completely vaporize, and the vessel is filled with vapor. The state at which this happens is represented by point E , which can be located by finding the temperature at which the saturated vapor density is equal to the fill density. Further heating beyond point E will only occur along the vapor isochore, EF , corresponding to the fixed ρ_{fill} . If ρ_{fill} is equal to ρ_c , heating will cause little change in the level of the meniscus because the rate of thermal expansion of the liquid is more or less balanced by its vaporization rate. The heating process will follow the saturation curve until the critical point C is reached where the meniscus disappears. Further heating then follows the critical isochore, CG . Note that the critical isochore has the same slope as the saturation curve at the critical point. Figure 1 clearly illustrates the undesirable feature of heating the vessel beyond the liquid-full condition because a small increase in temperature can create a dangerous over-pressure large enough to rupture the vessel.

2.2.1 Pure Agents. The experimental set-up is shown in Figure 2. A stainless steel (SS 304) vessel was used to measure the pressure-temperature relationship of the eleven agents. The vessel was tested hydrostatically to 20.6 MPa (3000 psia).

A K-type thermocouple (Omega TJ36-CASS-116U-12) was inserted into the vessel to monitor the internal temperature of the vessel in order to ensure that thermal equilibrium was reached between the vessel interior and the ambience. For high temperature (150 °C) measurements, the vessel was immersed in a silicone oil bath heated with an immersion heater (Cole-Parmer Model L-01266-02). For low temperature measurements, the vessel was submerged in a heat transfer fluid (Dow Corning Syltherm XLT) which was cooled by two immersion coolers (NESLAB). One cooler (Model IBC-4A) had a cooling capacity between 20 °C and −30 °C whereas the other (Model CC100-II) had a capacity between −25 °C and −100 °C. The rationale for using two coolers was that the cooling time of the heat transfer fluid to the required temperature (−60 °C) was greatly reduced and that together with the immersion heater the entire temperature range, from −60 °C to 150 °C, was covered.

A pressure relief valve (Nupro Model 177-R3A-K1-E) with a relieve pressure of 15.5 MPa (2250 psig) was used in the experimental set-up to prevent any accidental pressure overshoot when the vessel was exposed to high ambient temperature. A pressure transducer (DRUCK Model PDCR 330) was used to measure the internal pressure of the vessel. The transducer had an accuracy of 6.9 kPa (1 psi) and an operating range from 0.101 MPa (14.7 psia) to 13.8 MPa (2015 psia).

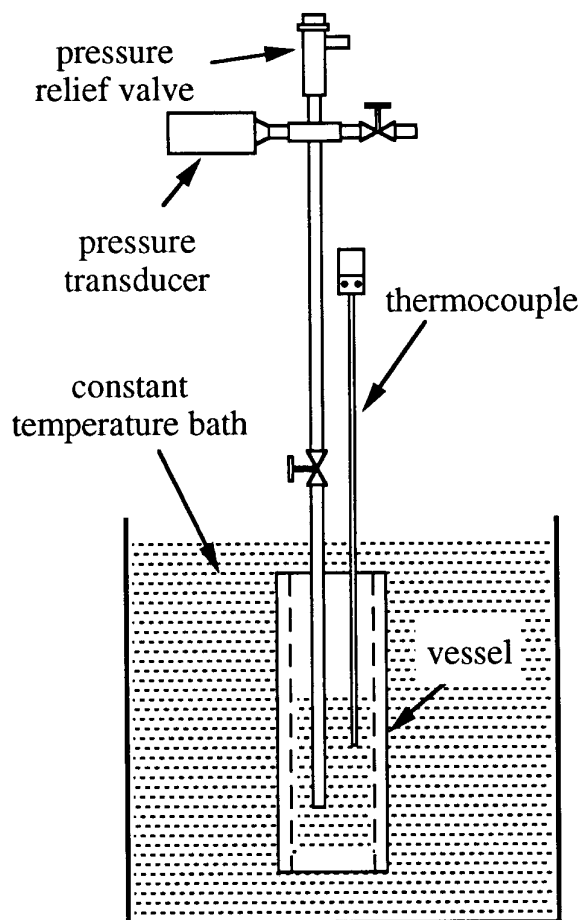


Figure 2. Schematic of temperature-pressure measurement experimental set-up.

There were two needle valves (Whitey SS-ORS2) in the apparatus. The one that was attached to the pressure vessel was used for filling and the other was used for isolating the apparatus from the vacuum pump line or the pressurization gas supply line.

The total internal volume of the experimental apparatus was determined as follows. For the vessel together with the attached needle valve, the internal volume was measured by filling them with de-ionized water and weighing them on an electronic scale with an accuracy of 0.1 g. After this volume was determined, the entire system (Figure 2) was evacuated for at least 5 minutes and pressurized with nitrogen to a fixed pressure at room temperature. The lower needle valve was then closed, confining nitrogen to the vessel. The nitrogen remaining in the rest of the system was bled out. With the lower needle valve closed, the apparatus was evacuated for at least 5 minutes by connecting a vacuum line to the upper needle valve. The upper needle valve was then closed before removal of the vacuum line from the apparatus. The lower needle valve was then fully opened, allowing the nitrogen in the vessel to expand throughout the apparatus. The final pressure of the set-up was recorded after thermal equilibrium with room temperature had been reached. Knowing the initial pressure (before expansion), the initial volume (lower needle valve together with the vessel), and the final pressure (after expansion), the total internal volume of the system was calculated by using the ideal gas law and was found to be $53.2 \pm 0.5 \text{ cm}^3$.

The experimental procedure was as follows. The vessel together with its needle valve was initially disconnected from the experimental set-up and evacuated for at least 5 minutes. The vessel was then connected to the agent supply bottle (not shown in Figure 2). By immersing the vessel in dry ice, liquid agent was dispensed through the needle valve into the vessel by condensing gaseous agent from the supply bottle. No attempt was made to remove noncondensable gases, if there were any, in the liquid agents. The amount of agent used in each of the experiments was approximately equal to the amount required to fill one-third of the vessel volume with liquid agent. The vessel was then weighed on an electronic balance with an accuracy of 0.1 g to determine the actual mass of the agent. The vessel was re-connected to the experimental set-up, which was then evacuated for at least 5 minutes before the needle valve attached to the vessel was opened fully. The apparatus was then immersed in the controlled temperature bath. The pressure of the vessel was recorded from the pressure transducer read-out when the internal temperature had reached thermal equilibrium with the bath temperature. Note that since FC-116 is a gas at room temperature, the 1/3 fill condition was not applicable to this agent. Although liquid FC-116 could still be dispensed by condensing gaseous FC-116 in the dry-ice-cooled vessel, this approach was not taken because the amount of liquid mass in the vessel could cause a huge pressure rise when the vessel was warmed back to room temperature. An average fill density of about 370 kg/m^3 was used for FC-116. This fill density was governed by the pressure of the agent supply bottle, *i.e.*, gaseous FC-116 was dispensed into the vessel directly from the supply bottle until an equilibrium pressure was reached in both the vessel and the supply bottle.

2.2.2 N_2 /Agent and CHF_3 /Agent Mixtures. As mentioned in the beginning of this section, the same experimental set-up for evaluating pure agents was used for the mixtures. The experimental procedure is described in the following paragraph.

After a pure liquid agent was dispensed in the vessel as described above and the vessel was re-connected to the experimental set-up, the pressurization gas supply line was then connected to the upper needle valve. The supply line together with the experimental set-up was evacuated for at least 5 minutes before initiating a slow flow of the pressurization gas. The lower needle valve was then fully opened to allow the gas to bubble slowly through the liquid agent until an equilibrium pressure of approximately 4.1 MPa (600 psia) was reached. Repetitive bubbling of the pressurization gas was required before the final equilibrium pressure could be obtained. This value of pressure was selected

in order to simulate a charging pressure commensurate with existing halon 1301 vessel. The vessel was then immersed in the controlled temperature bath. Once the vessel was in thermal equilibrium with the bath, the pressure of the vessel was recorded.

2.2.3 Solubility of N₂ and CHF₃ in Agents. Figure 3 shows a schematic of the apparatus used for solubility measurements. The experimental apparatus included the same stainless steel vessel used in the pressure-temperature measurements, a needle valve for dispensing the liquid agent and pressurization gas, a thermocouple, and a pressure transducer (DRUCK Model PDRR 330). The actual volume of the system was determined by pressurizing it with nitrogen to 4.02 MPa and then weighing it on an electronic scale with an accuracy of 0.1 g. Knowing the temperature, the pressure, and the mass of nitrogen, the volume was then calculated by using a generalized correlation for the compressibility factor (Smith and Van Ness, 1975). The total volume of the apparatus was found to be $53.9 \pm 0.6 \text{ cm}^3$.

The experimental procedure was as follows. The apparatus was evacuated for at least 5 minutes before the agent was dispensed to the vessel. The same filling and pressurization procedure were used as in the pressure-temperature measurements for mixtures. After pressurization with nitrogen or CHF₃, the amount of pressurization gas required to pressurize the vessel to the specified final pressure was then obtained by weighing the apparatus. This amount corresponded to the sum of the mass of nitrogen or CHF₃ in the vapor phase and that of the dissolved nitrogen or CHF₃ in the liquid agent.

2.3 Results and Discussion

2.3.1 Pure Agents. Table 3 summarizes the results (averages of at least two runs \pm half the range) of temperature-pressure measurements for pure agents at $150 \pm 1 \text{ }^\circ\text{C}$. Fill density is defined as the ratio of the mass of the agent to the volume of the apparatus (53.2 cm^3). The third column shows the measured final pressures at $150 \pm 1 \text{ }^\circ\text{C}$. For all the agents evaluated, the final pressures at $150 \text{ }^\circ\text{C}$ were less than 11 MPa (1600 psia). At $-60 \text{ }^\circ\text{C}$, the final pressures for all the agents, except HFC-27ea and FC-116, were below 0.101 MPa (14.7 psia) which is below the measuring range of the pressure transducer. For FC-116, an average final pressure of 0.25 MPa was found at $-61 \text{ }^\circ\text{C}$. For HFC-227ea, an average final pressure of 0.18 MPa was measured at $-60 \text{ }^\circ\text{C}$. Subsequent measurements of HFC-227ea from a different agent bottle showed an average value below 0.101 MPa. The results of HFC-227ea reported herein were obtained by using the agent supply bottle that gave a final pressure of 0.25 MPa at $-60 \text{ }^\circ\text{C}$, which represented the worst case.

Since the amount of agent and the volume of the apparatus (53.2 cm^3) were constant, an existing equation of state was used to predict the final pressure at the final temperature along an isochore or constant density line. The Peng-Robinson equation of state (Peng and Robinson, 1976) has recently been used to correlate thermodynamic properties of refrigerants and their mixtures (Abu-Eishah, 1991). It is given by

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \quad (1)$$

where v is the molar volume, R is the universal gas constant, and T is the absolute temperature (in K). The parameters a and b are given in terms of the reduced temperature ($T_R \equiv T/T_c$), and the acentric factor, ω :

Table 3. Comparison of measured pressures at 150 ± 1 °C with calculated values from REFPROP and the Peng-Robinson equation of state

Agent	Fill density (kg/m ³)	P_f (MPa) measured	P_f (MPa) REFPROP	error ^a (%)	P_f (MPa) P-R EOS	error ^b (%)
HFC-236fa	467 ± 2.0	4.50 ± 0.03	-	-	4.24	5.8
FC-31-10	523 ± 0	3.45 ± 0.01	-	-	3.76	9.0
FC-318	526 ± 1.1	4.05 ± 0.01	4.31	6.7	4.40	8.6
HCFC-124	471 ± 2.4	4.93 ± 0	5.22	5.9	5.27	6.9
HFC-227ea	495 ± 1.3	5.13 ± 0.04	5.27	2.7	5.41	5.5
CF ₃ I	733 ± 0.1	5.19 ± 0.01	-	-	6.06	16.8
HFC-134a	430 ± 0.8	6.80 ± 0.02	7.53	10.7	7.73	13.7
FC-218	500 ± 3.5	5.41 ± 0.02	5.89	8.9	6.11	12.9
HCFC-22	436 ± 2.7	8.48 ± 0.13	9.25	9.1	9.48	11.8
HFC-125	456 ± 1.2	7.73 ± 0.07	8.60	11.3	8.90	15.1
HFC-32/125	390 ± 0.5	10.78 ± 0.07	-	-	12.67	17.5
CF ₃ Br	605 ± 0.3	8.11 ± 0	-	-	9.07	11.8
FC-116	368 ± 5.9	6.77 ± 0.10	-	-	7.70	13.7

$$^a\text{error (\%)} = |P_f(\text{measured}) - P_f(\text{REFPROP})| \times 100/P_f(\text{measured})$$

$$^b\text{error (\%)} = |P_f(\text{measured}) - P_f(\text{P-R EOS})| \times 100/P_f(\text{measured})$$

$$a(T) = a(T_c) \alpha(T_R, \omega) \quad (2)$$

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (3)$$

$$\alpha = [1 + \beta(1 - T_R^{1/2})]^2 \quad (4)$$

$$\beta = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \quad (5)$$

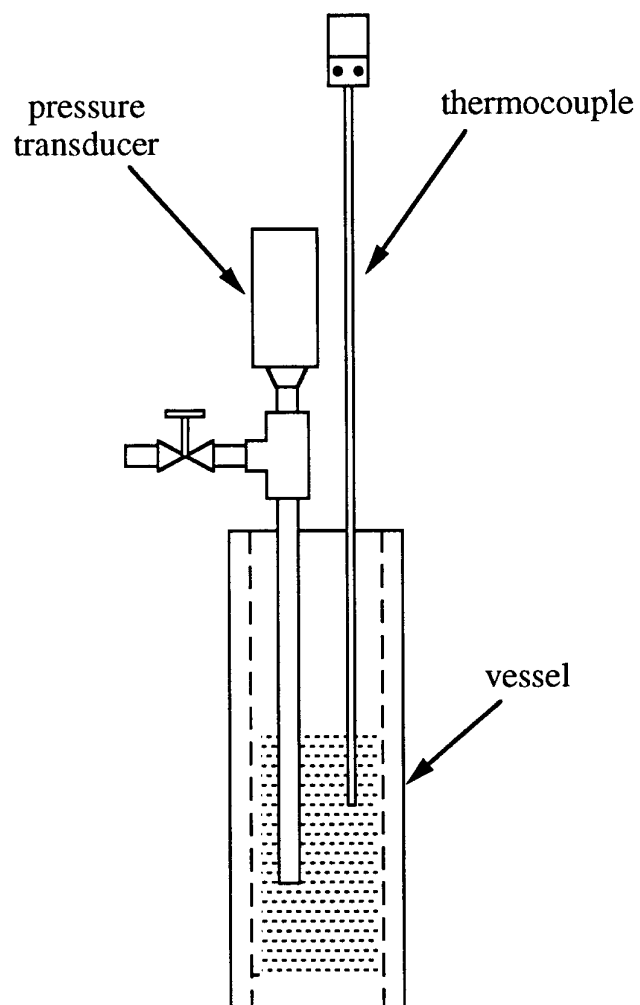


Figure 3. Experimental set-up for solubility measurement.

$$\omega = -\log\left(\frac{p_{sat}}{P_c}\right)_{T/T_c = 0.7} - 1.000 \quad (6)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (7)$$

In addition, the computer program, REFPROP (Gallagher *et al.*, 1993) was used to compare with the calculated results obtained by using the Peng-Robinson equation of state. REFPROP was developed by using the Carnahan-Starling-DeSantis equation of state (Morrison and McLinden, 1986):

$$\frac{Pv}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a^*}{RT(v + b^*)} \quad (8)$$

$$y = \frac{b^*}{4v} \quad (9)$$

$$a^* = a_0 \exp(a_1 T + a_2 T^2) \quad (10)$$

$$b^* = b_0 + b_1 T + b_2 T^2 \quad (11)$$

where a_0 , a_1 , a_2 , b_0 , b_1 , and b_2 are parameters obtained from fitting of limited experimental data. Table 3 also summarizes the results obtained from REFPROP and the Peng-Robinson equation of state (P-R EOS). The calculations were based on the conditions (average values) given in the second and third columns in Table 3. The blank entries in Table 3 imply that those agents are not currently included in REFPROP.

From Table 3, it appears that REFPROP predicts the final pressures much closer to the experimental values than the Peng-Robinson equation of state. In all cases, except for HFC-236fa, both equations of state tend to overestimate the final pressures.

2.3.2 N₂/Agent and CHF₃/Agent Mixtures. Table 4 tabulates the results (averages of at least two runs \pm half the range) of N₂/agent mixtures. The third column shows the initial pressures of the vessel at 23 ± 1 °C, the fourth column lists the final pressures of the vessel when the temperature is at -60 ± 1 °C, and the fifth column tabulates the final pressures of the vessel at 150 ± 1 °C.

At -60 °C, there was still significant residual pressure in the vessel. This residual pressure was mainly due to the nitrogen in the vapor phase because the contribution to the pressure from the agent vapor was insignificant due to very low vapor pressure (< 0.101 MPa) of the agent at -60 °C. Therefore, the initial pressurization of the vessel with nitrogen ensures that enough residual driving force to propel the agent out of the vessel is still present when the vessel is discharged at a cold ambience. Without the pressurization gas, the vapor pressure of the agent was so low that the only

driving force was the static head of the liquid agent when the vessel was placed in the vertically downward position.

At 150 °C, the final pressures of all the agents, with the exception of the HFC-125/HFC-32 mixture, were below 13.7 MPa (2000 psia). For the mixture, the experiment was terminated at 140 °C because the pressure was close to exceeding the operating range of the pressure transducer.

The results of CHF₃/agent mixtures are summarized in Table 5. The explanation of the content of the table is similar to that of Table 4. The values shown in Table 5 are the averages of at least two runs with their half range.

At about -60 °C, the final residual pressures in all cases were very low. This would make CHF₃ as a pressurization gas unfavorable if the vessels were to be discharged at low temperatures. The results also imply that a significant amount of CHF₃ was dissolved in the liquid agent at -60 °C.

When the agent/CHF₃ mixtures (except FC-116/CHF₃) were heated, the pressures exceeded 13.7 Pa by the time a temperature of 70 °C had been reached. Because CHF₃ is highly soluble in all the liquid agents and the initial amount of CHF₃ required to pressurize the vessel is very significant (see Section 2.3.3), an increase in pressure at moderately elevated temperatures was caused by a decrease in solubility of CHF₃ in the liquid agent and a subsequent increase in the amount of CHF₃ in the ullage. As a result, if CHF₃ were to be selected as a pressurization gas, extreme care should be taken in the design of the bottle for the replacement agent, especially if the bottle is to be exposed to a high temperature environment.

2.3.3 Solubility of N₂ and CHF₃ in Agents.

2.3.3.1 Experimental Results. Table 6 summarizes the experimental results (averages of at least two runs \pm half the range) for nitrogen. In all cases, the total amount of nitrogen required to pressurize the system to 4.1 MPa was less than 8% of the total mass of the agent.

Experimental results (averages of at least two runs \pm half the range) from CHF₃/agent mixtures are shown in Table 7. The amount of CHF₃ needed to pressurize the vessel to \sim 4.1 MPa is as much as or greater than that of the agent in the vessel. This is not surprising because CHF₃ is readily soluble in all the agents. Since a significant amount of CHF₃ is dissolved in the liquid agent, subsequent heating of the vessel causes a steep rise in pressure due to decreasing solubility of CHF₃ in the liquid agent at high temperatures (see Section 2.3.2).

2.3.3.2 Theoretical Predictions. In order to determine the solubility of nitrogen in the agent, measurements of nitrogen and agent concentrations in both phases are required. Solubility is normally defined as the mole fraction of nitrogen dissolved in the liquid agent. The present experimental set-up does not have the provision for sampling the liquid and gas phases, but the mass of nitrogen that is dissolved in the liquid agent can be estimated by applying mass balances on the agent and nitrogen. The calculation procedure is as follows.

Initially, the vessel is filled with a pre-determined amount of agent, $m_{a,t}$, at temperature T (K) (in this case room temperature); which is expressed as

$$m_{a,t} = m_{a,v} + m_{a,l} = \rho_{a,v} V_v + \rho_{a,l} V_l \quad (12)$$

where m is the mass, subscript t represents total, subscript a represent agent, subscripts v and l represent vapor and liquid phases respectively, ρ is the saturation density of the agent, and V is the volume. Since $m_{a,t}$, V_t , $\rho_{a,v}$, and $\rho_{a,l}$ are known and $V_l = V_t - V_v$, the masses of agent in both liquid and vapor phases can be calculated by substituting $V_t - V_v$ for V_l and solving for V_v in Equation (12).

Table 4. Initial pressures (P_i) at 23 ± 1 °C and final pressures ($P_{f,1}$) and ($P_{f,2}$) at -60 ± 1 °C and 150 ± 1 °C, respectively, for N_2 /agent mixtures

Agent	Fill density (kg/m ³)	P_i (MPa)	$P_{f,1}$ (MPa)	$P_{f,2}$ (MPa)
HFC-236fa	468 ± 0.2	4.16 ± 0	2.72 ± 0	9.66 ± 0.02
FC-31-10	523 ± 0.1	4.15 ± 0.02	2.68 ± 0.01	8.82 ± 0.03
FC-318	524 ± 2.3	4.16 ± 0.04	2.80 ± 0.18	9.32 ± 0.28
HCFC-124	471 ± 0.5	4.16 ± 0.05	2.65 ± 0	9.96 ± 0.02
HFC-227ea	492 ± 2.0	4.14 ± 0.02	2.55 ± 0.02	9.99 ± 0.10
CF ₃ I	736 ± 1.0	4.17 ± 0.01	2.67 ± 0	10.25 ± 0.01
HFC-134a	430 ± 0.5	4.16 ± 0.01	2.50 ± 0.01	11.59 ± 0.02
FC-218	497 ± 2.9	4.24 ± 0.05	2.40 ± 0.06	10.16 ± 0.44
HCFC-22	433 ± 0.3	4.20 ± 0.02	2.46 ± 0.01	13.00 ± 0.03
HFC-125	458 ± 1.2	4.16 ± 0.05	2.11 ± 0.04	11.59 ± 0.71
HFC-32/125	390 ± 2.9	4.13 ± 0.02	2.04 ± 0.01	$13.82^a \pm 0$
CF ₃ Br	601 ± 1.8	4.20 ± 0	2.07 ± 0	12.30 ± 0.04
FC-116	371 ± 0.9	4.24 ± 0.04	1.24 ± 0.02	9.07 ± 0.08

^aat 140 °C

$$V_v = \frac{m_{a,t} - \rho_{a,t} V_t}{\rho_{a,v} - \rho_{a,t}} \quad (13)$$

The vessel is then pressurized with nitrogen until an equilibrium pressure P_t at T is reached. Assuming that the dissolved nitrogen would not cause a significant change in the saturation liquid density of the agent and that the liquid agent is incompressible, the liquid mixture density can be approximated by the saturation liquid density of the pure agent. This approximation is reasonable if the amount of nitrogen dissolved in the liquid agent is much smaller than the mass of the liquid agent. If the vapor phase is further assumed to be ideal, then the total pressure P_t is given by

$$P_t = p_a + p_g \quad (14)$$

where p_a and p_g are the partial pressures of the agent and nitrogen respectively. From Raoult's law (Denbigh, 1984),

Table 5. Initial pressures (P_i) at 23 ± 1 °C and final pressures ($P_{f,1}$) and ($P_{f,2}$) at -60 ± 1 °C and $T_{f,2}$, respectively, for CHF₃/agent mixtures

Agent	Fill density (kg/m ³)	P_i (MPa)	$P_{f,1}$ (MPa)	$T_{f,2}$ (°C)	$P_{f,2}$ (MPa)
HFC-236fa	467 ± 1.0	4.19 ± 0.07	0.30 ± 0.01	48 ± 1	13.51 ± 0.01
FC-31-10	523 ± 0.4	4.31 ± 0.01	0.33 ± 0.01	56 ± 0	13.50 ± 0.01
FC-318	525 ± 0.6	4.21 ± 0.01	0.34 ± 0	53 ± 1	13.53 ± 0.02
HCFC-124	472 ± 0.5	4.11 ± 0.01	0.29 ± 0	48 ± 1	13.55 ± 0.02
HFC-227ea	495 ± 0.6	4.22 ± 0.02	0.29 ± 0	53 ± 1	13.51 ± 0.03
HFC-134a	426 ± 0.4	4.18 ± 0.05	0.27 ± 0	47 ± 1	13.55 ± 0.03
FC-218	498 ± 1.8	4.19 ± 0.02	0.44 ± 0.04	62 ± 0	13.54 ± 0.01
HCFC-22	433 ± 0.1	4.21 ± 0.05	0.29 ± 0.01	49 ± 1	13.53 ± 0.03
HFC-125	455 ± 0.5	4.23 ± 0.04	0.28 ± 0.01	52 ± 1	13.58 ± 0.01
HFC-32/125	391 ± 1.1	4.19 ± 0.02	0.27 ± 0.01	51 ± 3	13.59 ± 0.11
FC-116	376 ± 1.5	4.21 ± 0.08	0.39 ± 0.02	150 ± 0	11.22 ± 0.70

$$p_a = x_{a,l} p_{sat} = \frac{n_{a,l}}{n_{g,l} + n_{a,l}} p_{sat} \quad (15)$$

where $x_{a,l}$ is the mole fraction of the agent in the liquid phase, p_{sat} is the saturation vapor pressure of the agent at temperature T , $n_{g,l}$ is the number of moles of dissolved gas in the liquid phase, and $n_{a,l}$ is the number of moles of agent in the liquid phase. Furthermore, p_g can be calculated by

$$p_g = \frac{n_{g,v} RT}{V_v} = \frac{(n_{g,t} - n_{g,l}) RT}{V_v} \quad (16)$$

where $n_{g,v}$ is the number of moles of pressurization gas in the vapor phase, $n_{g,t}$ is the total moles of pressurization gas required to pressurize the vessel to P_t at a temperature T , and R is the universal gas constant. Substituting Equations (15) and (16) into Equation (14), a quadratic equation for $n_{g,l}$ (unknown) is obtained.

$$n_{g,l}^2 + n_{g,l} (n_{a,l} - n_{g,t} + \frac{P_t V_v}{RT}) + n_{a,l} (\frac{P_t V_v}{RT} - \frac{p_{sat} V_v}{RT} - n_{g,t}) = 0 \quad (17)$$

Solving for $n_{g,l}$ (only one root is meaningful) and knowing $n_{g,v} = n_{g,t} - n_{g,l}$, the amount of nitrogen in both phases can be calculated. When no nitrogen is dissolved in the liquid agent (*i.e.*, $n_{g,l} = 0$), $P_t = p_g + p_{sat}$ is recovered from Equation (17).

Table 6. Amount of nitrogen required to pressurize mixture to total pressure, P_t at 23 ± 1 °C

Agent	P_t (MPa)	Nitrogen (g)	Agent (g)
HFC-236fa	4.27 ± 0.08	1.9 ± 0.1	24.8 ± 0.1
FC-31-10	4.15 ± 0.02	2.0 ± 0	27.8 ± 0.1
FC-318	4.16 ± 0.03	2.0 ± 0.1	28.0 ± 0
HCFC-124	4.16 ± 0.01	1.9 ± 0.1	25.2 ± 0.1
HFC-227ea	4.16 ± 0	1.8 ± 0	26.3 ± 0.1
CF ₃ I	4.28 ± 0.05	1.9 ± 0	39.0 ± 0
HFC-134a	4.18 ± 0.02	1.8 ± 0.1	22.8 ± 0.1
FC-218	4.15 ± 0.02	1.7 ± 0.1	26.6 ± 0.1
HCFC-22	4.12 ± 0.01	1.4 ± 0.1	21.4 ± 0.1
HFC-125	4.21 ± 0.14	1.5 ± 0.1	24.3 ± 0
HFC-32/125	4.17 ± 0.01	1.3 ± 0	20.7 ± 0.1
CF ₃ Br	4.17 ± 0.01	1.4 ± 0.1	32.0 ± 0.1

The results and the parameters that are required to perform the calculation are shown in Table 8. The conditions used for the calculations correspond to Table 6. The calculated solubilities ($x_{g,l}$) and mass fractions ($w_{g,l}$) are also tabulated in Table 8. Solubility is defined as follows:

$$x_{g,l} = \frac{n_{g,l}}{n_{g,l} + n_{a,l}} \quad (18)$$

and the mass fraction of nitrogen in the liquid agent is calculated by

$$w_{g,l} = \frac{x_{g,l}M_g}{x_{g,l}M_g + (1 - x_{g,l})M_a} \quad (19)$$

where M_a and M_g are the molecular weights of agent and pressurization gas (nitrogen) respectively.

For all the agents studied, the amount of nitrogen dissolved in the liquid agent was calculated to be less than 25% of the total amount of nitrogen added, and less than 2% of the mass of the agent.

The solubility of nitrogen in liquid agent can also be estimated if the solution can be assumed regular. A correlating scheme based on the theory of regular solutions and the law of corresponding states to predict solubility of a gas in liquid was developed by Prausnitz and Shair (1961). The following equations form the basis of the correlation of gas solubilities:

Table 7. Amount of CHF₃ required to pressurize mixture to total pressure, P_t at 23 ± 1 °C

Agent	P_t (MPa)	CHF ₃ (g)	Agent (g)
HFC-236fa	4.29 ± 0.04	32.8 ± 0	24.7 ± 0.1
FC-31-10	4.16 ± 0	28.8 ± 0.2	27.9 ± 0.1
FC-318	4.17 ± 0.01	30.3 ± 0	27.9 ± 0.1
HCFC-124	4.21 ± 0.05	32.0 ± 0.1	25.1 ± 0.1
HFC-227ea	4.16 ± 0.04	30.4 ± 0	26.3 ± 0.1
HFC-134a	4.17 ± 0.03	31.9 ± 0.1	22.7 ± 0
FC-218	4.23 ± 0.03	25 ± 0.1	26.4 ± 0
HCFC-22	4.33 ± 0.21	30.8 ± 0.4	22.8 ± 0
HFC-125	4.16 ± 0.01	28.2 ± 0	24.4 ± 0.1
HFC-32/125	4.20 ± 0.01	29.9 ± 0.1	20.7 ± 0.1
CF ₃ Br	4.12 ± 0.01	23.9 ± 0.1	31.8 ± 0.3

$$\frac{1}{x_{g,l}} = \frac{f_{pure,g}^L}{f_g^G} \exp\left[\frac{v_g^L (\delta_a - \delta_g)^2 \Phi_a^2}{RT} \right] \quad (20)$$

with

$$\Phi_a = \frac{x_{a,l} v_a^L}{x_{a,l} v_a^L + x_{g,l} v_g^L} \quad (21)$$

$$\delta_a \approx \sqrt{\frac{(h_{fg})_a - RT}{v_a^L}} \quad (22)$$

Table 8. Parameters used in the solubility calculations, calculated mass of nitrogen in liquid agents, calculated nitrogen solubility, and calculated nitrogen mass fractions in liquid agents (conditions shown in Table 6)

Agent	$\rho_{a,l}$ (kg/m ³)	$\rho_{a,v}$ (kg/m ³)	p_{sat} (MPa)	$m_{g,l}$ (g)	$x_{g,l}$	$w_{g,l}$
HFC-236fa	1371	15.8 ^a	0.26	0.2	0.05	0.01
FC-31-10	1505	27.3	0.25	0.4	0.11	0.01
FC-318	1504	27.0	0.30	0.4	0.10	0.02
HCFC-124	1363	22.5	0.36	0.3	0.06	0.01
HFC-227ea	1400	36.3	0.45	0.3	0.07	0.01
CF ₃ I	2102	36.7 ^a	0.46 ^b	0.3	0.06	0.01
HFC-134a	1214	30.2	0.62	0.3	0.05	0.01
FC-218	1333	83.4	0.84	0.3	0.08	0.01
HCFC-22	1206	40.7	0.96	N.S.	-	-
HFC-125	1201	84.0	1.31	0.3	0.05	0.01
HFC-32/125	1045	59.3	1.63	0.2	0.02	0.01
CF ₃ Br	1556	126.6	1.53	0.3	0.05	0.01

^aEstimated by using the ideal gas law

^bEstimated by the method of Lee and Kesler (Reid *et al.*, 1987)

N.S.: not significant

and

$$\delta_g \approx \sqrt{\frac{(h_{fg})_g - RT}{v_g^L}} \quad (23)$$

where f is the fugacity, v^L is the molar "liquid" volume, δ_g is the solubility parameter of solute (nitrogen), δ_a is the solubility parameter of solvent (liquid agent), h_{fg} is the heat of vaporization, superscripts L and G represent liquid and vapor phases respectively, and subscripts a and g represent agent and pressurization gas respectively. In order to use Equation (20) to estimate solubility, the three parameters for the dissolved gas as a hypothetical liquid ($f_{pure,g}^L$, v_g^L , and δ_g) need to be specified. These parameters are all dependent on temperature; however, according to the theory of regular solutions the term $v_g^L (\delta_a - \delta_g)^2 \Phi_a^2$ is not temperature-dependent. Therefore, any convenient reference temperature can be used for v_g^L and δ_g as long as the same reference temperature is also used for δ_a and v_a^L . Since the "liquid" molar volume and solubility parameters for gaseous solutes are normally tabulated at 25 °C in the literature, this temperature is used in the following calculation of

$v_g^L (\delta_a - \delta_g)^2 \Phi_a^2$. However, the dependence of the fugacity of the hypothetical liquid on temperature must be considered in the solubility estimation.

By applying the theorem of corresponding states, it can be shown that the reduced fugacity ($f_{pure,g}^L/P_{c,g}$) of the hypothetical pure liquid solute can be correlated as a universal function of the reduced temperature, $T/T_{c,g}$ (Prausnitz and Shair, 1961), where $P_{c,g}$, T and $T_{c,g}$ are the solute critical pressure, the solution temperature and the solute critical temperature respectively. The function can be represented by the following two equations (Walas, 1985):

$$\ln\left(\frac{f_{pure,g}^L}{P_{c,g}}\right) = 7.81 - \frac{8.06 T_{c,g}}{T} - 2.94 \ln\left(\frac{T}{T_{c,g}}\right) \quad 0.7 \leq \frac{T}{T_{c,g}} \leq 2.5 \quad (24)$$

$$f_{pure,g}^L \approx 6.0 \quad 2.5 < \frac{T}{T_{c,g}} \leq 3.0 \quad (25)$$

The correlation given by Prausnitz and Shair (1961) is for a total pressure (P_t) of 0.101 MPa. To account for higher pressure, the Poynting correction (Prausnitz *et al.*, 1986) should be applied; thus

$$f_{pure,g}^L (@ P_t) = f_{pure,g}^L (@ 0.101 \text{ MPa}) \exp \left[\frac{v_g^L (P_t - 0.101)}{RT} \right] \quad (26)$$

where P_t is in MPa.

Since Φ_a contains $x_{g,l}$, iteration is required to solve for $x_{g,l}$ in Equation (20). However, the iteration converges rapidly. If the solubility is small, a first approximation of $x_{g,l}$ can be obtained by setting Φ_a equal to unity.

The fugacity, f_g^G , is approximated by the partial pressure of nitrogen in the vapor phase and can be estimated as follows. From Equation (15),

$$f_g^G \approx p_g = P_t - p_a \quad (27)$$

$$f_g^G \approx P_t - (1 - x_{g,l})P_{sat} \quad (28)$$

Table 9 lists the parameters used in the solubility estimation and the calculated solubilities ($x_{g,l}$). The solubility parameters of the agents were obtained from Daubert and Danner (1992) or were calculated by using Equation (22) with v_a^L assumed to be the molar liquid volume of pure agent at 25 °C. The solubility parameter of nitrogen and v_g^L were obtained from Prausnitz *et al.* (1986).

The third method for predicting solubility is to perform a detailed vapor-liquid equilibrium calculation by using an appropriate equation of state. Specifically, an isothermal flash calculation is required (Prausnitz *et al.*, 1980, 1986, and Walas, 1985). Such calculations involve the determination of vapor and liquid phase compositions, given the total system composition (in this case, the amount of pressurization gas and the agent in the vessel, total pressure, and temperature). The computer program PROZPER developed by Ely and Huber (1993), was used to calculate the solubility of nitrogen in agents. The Peng-Robinson equation of state was used in the calculation although other

Table 9. Parameters used in the estimation of solubilities, calculated solubilities of nitrogen in agents, and calculated mass fractions of nitrogen in agents

Agent	v^L (cm ³ /mole) @ 25°C	δ (J/cm ³) ^{1/2} @ 25°C	$x_{g,l}$	$w_{g,l}$
HFC-236fa	111.4	12.9	0.18	0.04
FC-31-10	159.0	11.9	0.18	0.03
FC-318	133.4	13.0	0.18	0.03
HCFC-124	100.6	13.1	0.17	0.04
HFC-227ea	121.9	11.5	0.17	0.03
CF ₃ I	93.2	13.0	0.17	0.03
HFC-134a	84.6	13.5	0.16	0.05
FC-218	142.1	12.3	0.16	0.03
HCFC-22	72.4	17.3	0.14	0.05
HFC-125	100.9	10.2	0.14	0.04
HFC-32/125	64.7	13.0	0.12	0.05
CF ₃ Br	96.8	14.5	0.13	0.03
Nitrogen	32.4	5.3	-	-

equations of state could be used with some modification. Calculations were performed without taking the binary interaction coefficient into account.

Table 10 shows the input parameters used for the calculation by PROZPER and the calculated solubility. Agents that are not currently included in PROZPER have blank entries in the table. The column, $x_{g,t}$, represents the overall mole fraction of nitrogen in the vessel:

$$x_{g,t} = \frac{n_{g,t}}{n_{g,t} + n_{a,t}} \quad (29)$$

where $n_{g,t}$ and $n_{a,t}$ are the total moles of pressurization gas required and agent in the vessel, respectively, (given in Table 6), and $x_{a,t}$ ($= 1 - x_{g,t}$) is the overall mole fraction of agent.

Table 11 compares the three methods used to estimate nitrogen solubility in the agents studied. The solubilities obtained from the correlation scheme appear to be higher than those obtained by PROZPER, and the values calculated by the mass balance method are generally lower than those obtained by correlations and vapor-liquid equilibrium calculations. However, all three methods predict solubility on the same order of magnitude, and the calculated mass fractions of nitrogen in liquid agents in all cases are less than or equal to 0.05. The discrepancy could be due to the assumptions invoked in both mass balance and correlation techniques. In the mass balance approach, the density of the mixture is approximated by the density of pure agent. This assumption is only true if $x_{g,l} \rightarrow 0$. On the other hand, the correlation scheme may not work well if the pressure is high or if the solution is not regular.

Table 10. Experimental parameters, calculated solubilities of nitrogen, and mass fraction of nitrogen in liquid agents

Agent	T (K)	P_t (MPa)	$x_{g,t}$	$x_{g,l}$	$w_{g,l}$
HFC-236fa	296	4.27	0.29	-	-
FC-31-10	296	4.15	0.38	-	-
FC-318	297	4.16	0.34	0.13	0.02
HCFC-124	296	4.16	0.27	0.09	0.02
HFC-227ea	297	4.16	0.29	0.12	0.02
CF ₃ I	296	4.28	0.25	0.09	0.01
HFC-134a	296	4.18	0.22	0.09	0.03
FC-218	296	4.15	0.30	0.15	0.03
HCFC-22	295	4.12	0.17	0.07	0.02
HFC-125	296	4.21	0.21	0.11	0.03
HFC-32/125	297	4.17	0.13	-	-
CF ₃ Br	296	4.17	0.19	0.09	0.02

The first two approximate methods, discussed above, for estimating solubility are not appropriate for calculating solubility of CHF₃ in liquid agents because the assumptions made in the calculations become invalid. Given the amount of CHF₃ and that of the agent at a specified temperature and pressure, the solubility of CHF₃ in the liquid agent can, in principle, be estimated by performing an isothermal flash calculation. However, since the critical point of CHF₃ is very close to the experimental condition (at room temperature, and ~ 4.1 MPa), attempts to use PROZPER to estimate the solubility of CHF₃ in the agents were unsuccessful, the reason being that the Peng-Robinson equation of state may not be able to represent the region near the critical point well.

2.4 Summary and Recommendations

A vessel filled 1/3 with liquid agent initially at room temperature increased in pressure as it was heated to 150 °C to a value below 11 MPa (1600 psia), for all of the pure compounds studied. The HFC-32/125 mixture had the highest final pressure, 10.78 MPa. When cooled to -61 °C, the pressure of all the agents except FC-116 dropped below the ambient (0.101 MPa). The final pressure of FC-116 was 0.25 MPa (37 psia).

The amount of nitrogen required to pressurize the vessel to 4.1 MPa (600 psia) accounted for less than 8% of the total mass of the agent. The calculated mass fractions of nitrogen dissolved in the liquid agents in all cases was less than 0.05. For N₂/agent mixtures, the final pressure of the vessel at 150 °C was less than 14 MPa (2040 psia), with the HFC-32/125 mixture again yielding the highest final pressure (13.8 MPa). The nitrogen in the mixture maintained an appreciable residual pressure

Table 11. Comparison of the three methods used to calculate solubilities of nitrogen in agents (conditions shown in Table 6)

Agent	$x_{g,l}$ (Mass balance)	$x_{g,l}$ (Correlation)	$x_{g,l}$ (PROZPER)
HFC-236fa	0.05	0.18	-
FC-31-10	0.11	0.18	-
FC-318	0.10	0.18	0.13
HCFC-124	0.06	0.17	0.09
HFC-227ea	0.07	0.17	0.12
CF ₃ I	0.06	0.17	0.09
HFC-134a	0.05	0.16	0.09
FC-218	0.08	0.16	0.15
HCFC-22	-	0.14	0.07
HFC-125	0.05	0.14	0.11
HFC-32/125	0.02	0.12	-
CF ₃ Br	0.05	0.13	0.09

of 1.24 MPa (180 psia) even when the vessel was cooled to -60°C . This residual pressure is essential when the vessel is discharged at a cold ambience.

Significant amounts of CHF₃ were needed to pressurize the vessel to 4.1 MPa because CHF₃ is readily soluble in all of the liquid agents studied. For all of the CHF₃/agent mixtures, pressures above 13.7 MPa (2000 psia) were reached for temperatures as low as 70°C . At -60°C , the final pressures dropped below 0.45 MPa (65 psia). This low pressure would make CHF₃ an unfavorable choice for a pressurization gas if discharge of the vessel happened at very cold temperatures.

The following recommendations are made to ensure the integrity of the storage vessel:

1. The current pressure vessels described in military specification MIL-C-22284A (proof pressure of 9.62 MPa and minimum burst pressure of 12.37 MPa) should not be used as drop-ins for any of the core alternative agents when the vessels are to be exposed to or stored at temperatures up to 150°C .
2. Trifluoromethane, CHF₃, should not be used as a pressurization gas. If discharge of the vessel is to occur at cold ambience, a very low residual pressure will exist, and at temperature in excess of 70°C , very high pressures could lead to rupture of the vessel.

2.5 References

- Abu-Eishah, S.L., "Calculation of Vapor-Liquid Equilibrium Data for Binary Chlorofluorocarbon Mixtures Using the Peng-Robinson Equation of State," *Fluid Phase Equilibria* 62, 41 (1991).
- Allied Signal Inc., *Selected Physical Properties: HCFC-123, HCFC-123a, HCFC-124, HFC-125, HFC-134, HFC-134a, and HFC-143a*, Allied Signal Inc., Buffalo Research Laboratory, Buffalo, New York, 1990.
- Allied Signal Inc., *Genetron® Products Technical Bulletin: R-32/125 Azeotrope*, Allied Signal Inc., Genetron® Products, Morristown, New Jersey, July 1991.
- ASHRAE Inc., *ASHRAE Thermodynamic Properties of Refrigerants*, ASHRAE Inc., New York, 1969.
- Braker, W., and Mossman, A.L., *Matheson Gas Data Book*, 6th ed., Matheson Gas Products, New Jersey, 1980.
- Brown, J.A., and Mears, W.H., "Physical Properties of n-Perfluorobutane," *J. Phys. Chem.* 62, 960 (1958).
- Daubert, T.E., and Danner, R.P., *Physical and Thermodynamic Properties of Pure Chemicals, Data Compilation*, Hemisphere Publishing Corporation, New York, 1992.
- Denbigh, K., *The Principles of Chemical Equilibrium*, Cambridge University Press, Cambridge, 1984.
- Ely, J., and Huber, M.L., *PROZPER*, personal communication with M.L. Huber (1993).
- Fang, F., and Joffe, J., "Thermodynamic Properties of Perfluoropropane," *J. Chem. Eng. Data* 11, 376 (1966).
- Gallagher J., McLinden, M., Huber, M., and Ely, J., *NIST Standard Reference Database 23: Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), Version 4.0*, U.S. Department of Commerce, Washington, DC 1993.
- Great Lake Chemical Corporation, *FM-200™: Environmentally Superior Fire Extinguishant for Total Flooding Applications*, Great Lake Chemical Corporation, West Lafayette, Indiana, May 1993.
- Kudchadker, A.P., Kudchadker, S.A., Shukla, R.P., and Patnaik, P.R., "Vapor Pressures and Boiling Points of Selected Halomethanes," *J. Phys. Chem. Ref. Data* 8, 499 (1979).
- Morrison, G., and McLinden, M.O., *Application of a Hard Sphere Equation of State to Refrigerants and Refrigerant Mixtures*, NBS Technical Note 1226, U.S. Department of Commerce, Washington, DC 1986.
- Peng, D.-Y., and Robinson, D.B., "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.* 15, 59 (1976).
- Piao, C., Sato, H., and Watanabe, K., "Thermodynamic Charts, Tables, and Equations for Refrigerant HFC-134a," *ASHRAE Transactions* 97, 268 (1991).
- Platzer, B., Polt, A., and Maurer, G., *Thermophysical Properties of Refrigerants*, Springer-Verlag, Berlin, 1990.
- Prausnitz, J.M., and Shair, F.H., "A Thermodynamic Correlation of Gas Solubilities," *AIChE Journal* 7, 682 (1961).
- Prausnitz, J.M., Anderson, T.F., Grens, E.A., Eckert, C.A., Hsieh, R., and O'Connell, J.P., *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*, Prentice-Hall, New Jersey, 1980.
- Prausnitz, J.M., Lichtenthaler, R.N., and Gomes de Azevedo, E., *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed., Prentice-Hall, New Jersey, 1986.
- Reid, R.C., Prausnitz, J.M., and Poling, B.E., *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York, 1987.

Shankland, I.R., Basu, R.S., and Wilson, D.P., "Thermophysical Properties of HCFC-124: An Environmentally Acceptable Refrigerant," *ASHRAE Transactions* 96, 317 (1990).

Sladkov, I.B., and Bogacheva, A.V., "Critical Parameters of Mixed Carbon Halides," *Zhurnal Prikladnoi Khimii* 64, 2435 (1991); 64, 2276 (1992) (English translation).

Smith, J.M., and Van Ness, H.C., *Introduction to Chemical Engineering Thermodynamics*, 3rd ed., McGraw-Hill, New York, 1975.

Walas, S.M., *Phase Equilibrium in Chemical Engineering*, Butterworth, Boston, 1985.

Yaws, C.L., Ni, H.M., and Chiang, P.Y., "Heat Capacities for 700 Compounds," *Chemical Engineering* 95(7), 91 (1988).